Journal of Alloys and Compounds 641 (2015) 119–126

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jalcom

Acetylene black incorporated layered copper sulfide nanosheets for high-performance supercapacitor

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ARTICLE INFO

Article history:
Received 25 December 2014
Received in revised form 8 April 2015
Accepted 11 April 2015
Available online 16 April 2015

Keywords:
Acetylene black
Layered copper sulfide nanosheets
Hybrid materials
High-performance supercapacitors
Electrode materials

ABSTRACT

Two-dimensional transition metal chalcogenides are attracting increasing attention in energy storage due to their unique structures and electronic properties. CuS has been demonstrated with a metal-like electronic conductivity and a high theoretical capacity. In this work, a facile strategy was reported for one-step synthesis of acetylene black (AB) incorporated layered CuS nanosheet via a simple solvothermal route. X-ray diffraction, Raman spectroscopy, scanning electron microscopy and transmission electron microscopy were used to investigate the morphologies and microstructures of the as-prepared materials. Electrochemical data showed that the CuS/AB composites displayed a high specific capacitance of 2981 F/g at 1.0 A/g and retained 64.6% (1924.5 F/g) at a high current density of 20 A/g, indicative of good rate capability. Furthermore, the composites retained approximately 92% of the initial specific capacitance after 600 cycles at a current density of 1.0 A/g, demonstrating good cycling stability. The outstanding electrochemical properties of the CuS/AB composite suggested that it had great potential for practical applications in high-performance supercapacitors and the present synthesis strategy maybe readily extended to the preparation of other composites based on CuS for potential applications in energy storage and conversion devices.

1. Introduction

The increasing environmental pollution, the rapid growth of the global economy and the depletion of fossil fuels have stimulated intensive research into energy storage and conversion from alternative energy sources [1]. Energy storage devices have been used in various applications such as hybrid electric vehicles, mobile electronic devices and memory backup systems. Among different energy storage devices, supercapacitor has been reported as a promising candidate because it has a higher power density than batteries and a higher energy density than conventional capacitors [2–4]. The performances of supercapacitors are largely dependent on the properties and structures of the electrode materials. The energy stored in supercapacitors is either capacitive (electrochemical double layer capacitors, EDLC) or pseudocapacitive (pseudocapacitors) in nature, or both [5–7]. The capacitive process of EDLC is based on charge storage mechanisms at the surface of the electrode/electrolyte interface, which is usually with carbon-based materials as active materials, while the pseudocapacitive process relies on redox reactions that occur in the electrode materials, which is with transition metal oxides (RuO_2, Co_3O_4, MnO_2, etc.) and hydroxides ($Ni(OH)_2$, $Co(OH)_2$, etc.) or conducting polymers as active materials [8–10].

Nanomaterials have been widely investigated [11,12], especially in energy storage fields. In pseudocapacitors, RuO_2 and other transition metal oxides (such as MnO_2) have been used as electrode materials due to their high specific capacitance. However, expensive nature of RuO_2 and poor electrical conductivity of MnO_2 (10^{-5}–10^{-6} S/cm) limit their applications [13,14]. Compared with these transition metal oxides, metal sulfides are abundant and cheap due to the existence of minerals in nature [15]. Moreover, many metal sulfides are good metallic conductors and also undergo redox transitions among different valence states of the metal ion [16]. Some metal sulfides, such as MoS_2 [17], NiS [18], BiS [19] and WS_2 [20], have been investigated as novel electrode materials for supercapacitors in view of their special structural properties and high theoretical capacities. CuS, an important transition metal sulfide, is a typical p-type semiconductor. It is inexpensive and abundant material with widespread applications as chemical sensors, Li-ion batteries, catalysts, solar cells and so on [21–23]. Several attempts have been made to explore CuS as an electrode material for lithium-ion batteries and supercapacitors due to its metal-like electronic conductivity (10^{-3} S/cm) and high theoretical capacity (561 mA h/g) [24–27].

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http://dx.doi.org/10.1016/j.jallcom.2015.04.075
0925-8388/

Recently, layered micro/nanostructures with their ultrahigh surface area, low density and surface permeability, have increasingly attracted research attention for the application in supercapacitors [28–32]. Layered CuS has been reported as electrode materials for supercapacitors [33,34]. However, their capacitance values and cycle stability are still not satisfactory for their practical applications. Therefore, it is important to develop new layered CuS composites electrode materials with a combination of low cost, larger capacitance and good electrochemical stability.

Acetylene black (AB) is a carbon material, which is made by the controlled combustion of acetylene in air under pressure [35]. It has feature of light mass with small specific gravity, strong absorption of electrolyte, stable chemical property, low cost and good conductivity, and has attracted much attention in the field of energy storage [36–38].

In this research, acetylene black incorporated layered CuS nanosheet was prepared through a simple solvothermal route. The obtained 3D CuS/AB composites with rough surfaces and layered structures increased the effective utilization of active materials throughout the whole electrode matrix and reduced the effective diffusion distance of protons and electrons, leading to excellent electrochemical performance.

2. Experimental

2.1. Synthesis of CuS/AB composites

The AB was first pretreated as follows: 1.0 g AB was dispersed in 200 mL concentrated nitric acid, and the mixture was then refluxed at 140 °C for 2 h. After cooling, the obtained black product was washed thoroughly with deionized water until the pH was 7, and then dried at 80 °C for 24 h.

CuS/AB composites were synthesized by a simple ethylene glycol-assisted solvothermal method. Typically, 0.48 g $Cu(NO_3)_2{\cdot}3H_2O$ was first dissolved in 30 mL ethylene glycol. Subsequently, 0.30 g thiourea was added. Then, 0.096 g of the pretreated AB was added in the mixture and stirred for 30 min. Next, the mixture was transferred to a 100 mL Teflon-lined stainless steel autoclave, sealed tightly, and heated at 150 °C for 24 h. After cooling to room temperature naturally, the product was collected by centrifugation, washed with deionized water and ethanol, and then dried in a vacuum oven at 60 °C for 12 h. For comparison, CuS nanosheets were synthesized without AB via the same route. The procedure for CuS/AB composites preparation is illustrated in Fig. 1.

2.2. Characterization

The transmission electron microscopy (TEM) imaging was conducted by Tecnai G220S-TWIN microscope (FEI Company, Netherlands), and the scanning electron microscopy (SEM) imaging was conducted by Hitachi S-4800 scanning electron microscope. The X-ray photoelectron spectra (XPS) were collected by AXIS ultra DLD (Shimadzu Kratos) with an X-ray source of monochromatic Al Ka under 15 kV and 10 mA. X-ray powder diffraction (XRD) pattern measurements were conducted by a Japan Rigaku D/Maxr-A X-ray diffractometer equipped with graphite monochromatized high-intensity Cu Kα radiation (λ = 1.54178 Å). Raman spectra were measured on a Renishaw Raman system model 1000 spectrometer (Gloucestershire, UK) with a 540 nm laser. The N_2 adsorption–desorption isotherms of the samples were measured by a NOVA 2000 (Quantachrome, USA) in order to determine the specific surface areas. The specific surface area was calculated from the Brunauer–Emmett–Teller (BET) plot of the nitrogen adsorption isotherm.

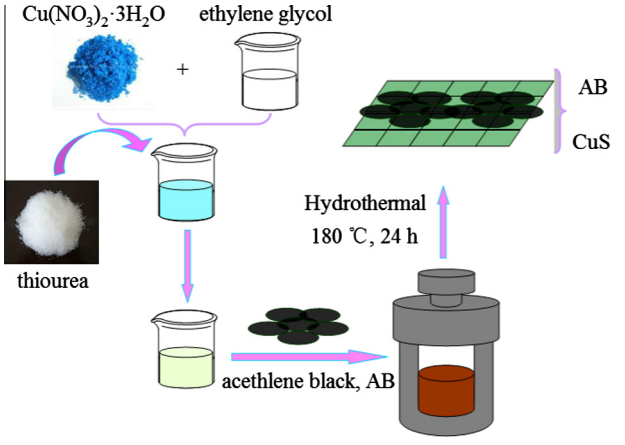

Fig. 1. Illustration of the procedure of the preparation of AB/CuS composites.

2.3. Electrochemical measurements

To prepare electrodes for electrochemical measurements, the active materials CuS/AB, poly(tetrafluoroethylene) binder and carbon black were mixed in a mass ratio of 75:15:10. Then the resulting slurry was coated onto the foam nickel substrate (1 cm × 1 cm). After the coated foam nickel was dried at 80 °C for 12 h in a vacuum, the working electrode was obtained, which contained about 0.75 mg CuS/AB composites. The cycle voltammetry (CV) and galvanostatic charge–discharge (GCD) measurements were performed in 6 M KOH aqueous solution by a CHI660E electrochemical station (Chenhua corp., Shanghai) using Hg/HgO as the reference electrode and Pt wire as the counter electrode. The electrochemical impedance spectroscopy (EIS) tests were carried out in frequency range from 0.01 to 100,000 Hz at the open circuit potential with an AC perturbation of 5 mV. The specific capacitances were calculated according to the following equation [39]:

$$C_s = It/\Delta Vm \quad (1)$$

where I, t, ΔV and m are the constant current (A), discharge time (s), the total potential difference (V) and the weight of active materials (g), respectively.

3. Results and discussion

3.1. Characterizations

SEM and TEM observations on the CuS, AB, and CuS/AB composites are presented in Fig. 2. As shown in Fig. 2A, the SEM imaging displays that the obtained CuS is composed of stacked plates; the plate is irregular in the diameter and less 20 nm in thickness. Generally, in the absence of external forces, the individual 2D nanosheets prefer to stack to form closed structures in order to decrease the number of dangling bonds and the total energy of the system. Further insight into the morphology and structure of the CuS nanosheets can be obtained through their TEM images as shown in Fig. 2D. It reveals the sample is a 2D thin-layer nanosheet. The SEM image of the as-prepared AB nanoparticles (Fig. 2B) exhibits uniform size, which is confirmed in Fig. 2E. Fig. 2C shows the representative SEM images of the CuS/AB composites. It shows the AB nanoparticles adhere closely on the surface of the CuS nanosheets. The TEM images of CuS/AB composites are shown in Fig. 2F and G. The AB nanoparticles are well distributed on CuS nanosheets, evidencing the well-behaved assembly process. The embedding of the AB on CuS nanosheets is help to improve the conductivity of CuS, meanwhile the unique properties of CuS nanosheets are retained.

The XRD patterns of CuS nanosheets, AB and CuS/AB products are shown in Fig. 3A. In the XRD pattern of AB, the peaks at 25.8 (002) and 42.7 (100) attribute to the hexagonal graphite structure (JCPDS card no. 34-1832). After AB incorporation, the XRD pattern of the composite displays almost the same diffraction peaks with pure CuS nanosheets. The absence of AB peaks indicates that AB uniformly disperses in the composites and is coated with CuS nanosheets. All the indexed peaks of CuS and CuS/AB composites in Fig. 3A can be assigned to CuS, and are in agreement with the standard diffraction data confirming the hexagonal phase crystalline structure of CuS (JCPDS card no. 06-0464). No characteristic peaks from impurities can be detected.

The presence of CuS, AB and CuS/AB composites was further confirmed by Raman spectroscopy. As shown in Fig. 3B, the peak at about 474 cm^{-1} corresponds to the A_{1g} mode of CuS nanosheets. The peaks observed at 1291 cm^{-1} and 1610 cm^{-1} are two major features of AB, which are corresponded to the D band and G band of carbon. The intensity ratio (I_D/I_G) of D-band to G-band for the CuS/AB composite is 1.34, which is higher than that of the pure AB (1.12). The increase of the I_D/I_G ratio can be partly attributed